

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau(43) International Publication Date
12 June 2003 (12.06.2003)

PCT

(10) International Publication Number
WO 03/049208 A2

(51) International Patent Classification⁷: **H01L 39/24**

(21) International Application Number: PCT/GB02/05527

(22) International Filing Date: 6 December 2002 (06.12.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data: 0129410.7 7 December 2001 (07.12.2001) GB

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(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- without international search report and to be republished upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

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(54) Title: MAGNESIUM DIBORIDE SUPERCONDUCTORS

(57) **Abstract:** A method of manufacturing polycrystalline bulk MgB₂ with enhanced superconducting properties, by introducing structural defects forming pinning sites for quantised magnetic vortices, so as to prevent them from moving under the action of the Lorentz force.

"Magnesium Diboride Superconductors"

Magnesium Diboride (MgB_2) was discovered to have superconducting properties
5 in early 2001 [1]. The pure material is a type II superconductor with a superconducting
transition temperature T_c of $\sim 39K$.

Magnesium Diboride falls between the classic low temperature superconductors
(LTS) e.g. NbTi and NbSn with T_c 's under $20^{\circ}K$, and the newer High Temperature
Superconductors (HTS) e.g. $YBaCuO$ and $BiSrCaCuO$ with T_c 's over $90^{\circ}K$.

10 LTS superconductors are most frequently operated at or near $4^{\circ}K$ using liquid
helium as a coolant. HTS superconductors have been targeted at an operating
temperature as high as $77^{\circ}K$ where liquid nitrogen could be used as the coolant.

Magnesium Diboride shows promise for use at about $20^{\circ}K$, where relatively inexpensive
closed cycle refrigerator cooling could be employed.

15 Unlike many of the HTS materials, supercurrent in the MgB_2 system is not
significantly hindered by grain boundaries. This means that long lengths of high
performance polycrystalline materials may be easier to fabricate. In addition, the starting
and sheathing materials of the MgB_2 conductor are less expensive than those involved
in the production of polycrystalline HTS conductors of the Bi based compounds, and
20 much more simple than for the HTS conductors of the RE based compounds. The
possibility of use at about $20^{\circ}K$, combined with the possible low cost in conductor
fabrication would make MgB_2 an attractive material for the Magnetic Resonance Imaging
market (MRI) operated on $20^{\circ}K$ cryocoolers, and other high current conductor
applications.

25 Fragments of the pure material have been shown to support critical current
density (J_c) of over $10^6 A/cm^2$ at $20^{\circ}K$ and zero applied field. However, in such
fragments the critical current density falls to values below $10^3 A/cm^2$ at relatively low

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fields of between 3.5 and 4 T at 20°K [2]. This fall off in the Jc in bulk material with applied field appears to be more rapid than it is in the HTS materials at the same temperature.

The magnitude and field dependence of Jc are related to the presence of
5 structural defects that can "pin" the quantised magnetic vortices that permeate the material and prevent them from moving under the action of the Lorentz force. Vortex studies suggest that it is the lack of suitable pinning sites in MgB₂ that causes the rapid decay of Jc with field. [2]

If the vortex pinning could be strengthened so as to increase Jc in magnetic
10 fields of a few Tesla then MgB₂ could compete both on price and performance with the HTS alternatives when operated at about 20°K.

It has been shown that low levels of atomic disorder, introduced by proton irradiation enhance the pinning and so increase Jc significantly at high fields. [3]

Irradiation is not a viable technique for large scale conductor fabrication.
15 Accordingly, the present application provides a method of enhancing the superconducting properties of polycrystalline bulk MgB₂ by modifying the process of manufacturing the material in such a way as to give rise to structural defects forming pinning sites for quantised magnetic vortices, so as to prevent them from moving under the action of the Lorentz force.

20 A first preferred method according to the present invention comprises the step of introducing specific chemical impurities, chosen on the basis of their ionic radius and ionic charge. Suitable materials include Si, Cu, Zn and Al, C, Li, and N

A second preferred method according to the present invention comprises the step of introducing particles of a material chosen for its nano-particle starting size. The
25 additive should be a material which remains in the same form after reaction, or

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something that reacts to form a nano-boride phase. A preferred material for this purpose is Y_2O_3 [4].

In the first preferred method, the additive is preferably introduced in nominal concentrations between 1% and 5% atomic percent during a solid state reaction 5 between Mg, B and the additive. Preferably the concentration is about 3 at.%. In the second preferred method, the additive is preferably introduced in concentration of 5-15 wt. %. Preferably the concentration is about 10 wt. %.

Preferably B, Mg and alloying additive are mixed, pressed into pellets and then sintered in an inert atmosphere (5% H_2 in Ar or in N/Ar) in a reaction which involves a 10 15-minute anneal at 900°C. Excess Mg is present in the reaction chamber to ensure the formation of MgB_2 .

A third preferred method according to the invention is characterised by the time of reaction and the precise form of the B starting precursor. MgB_2 made using commercially obtained amorphous B powder appears to yield a shallow dependence of 15 J_c on field, similar to the effect of the alloying additions and Y_2O_3 nano-particle additions. A short reaction time is also beneficial, with 15 minutes at 900°C better than longer reaction times (e.g. 60 minutes).

Figure 1 shows the form of the precipitates which result when 10 wt. % Y_2O_3 is reacted with the Mg+B. A nano-phase of YB_4 results in a very fine and even distribution. 20 The graph of Figure 2 shows the critical current J_c normalised by J_c at 2T field 20°K of the MgB_2 + various dopants measured using a magnetisation method. Also shown is the J_c behaviour for an undoped MgB_2 made by a standard reaction route as well as MgB_2 made by a rapid reaction route (15 min. 900°C) using an amorphous B precursor powder.

25 The graph shows the following different samples:

MgB_2 + 3 at. % Zn, MgB_2 + 3 at. % Cu, MgB_2 + 3 at. % Al, MgB_2

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MgB₂ + 10wt % Y₂O₃ nanoparticles

MgB₂ undoped sample made by a standard route (60min anneal at 900°C)

MgB₂ undoped sample made by a 'special' route (15min anneal at 900°C)

Because the pellets are not fully dense and unlikely to be fully connected it is not

5 possible to directly compare the exact values of J_c as obtained by the method of measurement. Hence the normalised method is more informative. What is of importance is the rate at which the J_c is being diminished with increasing field i.e. the gradient of the J_c(B) plot.

10 The addition of the dopants, and in particular the Al and the Y₂O₃, as well as rapid reaction of undoped material to induce disorder, prolongs to much higher fields the value at which J_c drops below 1000 A/cm². This suggests that the pinning has been strengthened considerably by the addition of the dopants.

[1] Nagamatsu, J., Nakagawa, N., Muranaka, Y., Zenitani, Y. & Akimitsu, J. Superconductivity in MgB₂. *Nature* 410, 63-64 (2001).

15 [2] Y. Bugoslavsky, G. K. Perkins, X Qi, L. F. Cohen, and A. D. Caplin. Vortex dynamics in superconducting MgB₂ and prospects for applications. *Nature* 410 563-565, 2001.

[3] Y. Bugoslavsky, L. F. Cohen, G. K. Perkins, M. Polichetti, T. J. Tate, R. Gwilliam, and A. D. Caplin. Enhancement of the high-magnetic-field critical current density of 20 superconducting MgB₂ by proton irradiation. *Nature* 411:561-563, 2001.

[4] J. Wang, Y. Bugoslavsky, A. Berenov, L. Cowey, A.D. Caplin, L.F. Cohen, J.L. MacManus-Driscoll, L.D. Cooley, X. Song, D.C. Larbalestier, " High Critical Current Density and Improved Irreversibility Field in Bulk MgB₂ Made by a Scaleable, Nanoparticle Addition Route, Applied Physics Letters 81 (11) 9 September 2002

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CLAIMS

1. A method of manufacturing polycrystalline bulk MgB₂ with enhanced superconducting properties, by introducing structural defects forming pinning sites for quantised magnetic vortices, so as to prevent them from moving under the action of the 5 Lorentz force.
2. A method according to claim 1 in which the structural defects are formed by including a specific chemical impurity chosen for its ionic radius and ionic charge.
3. A method according to claim 2 in which the impurity comprises one or more of Si, Cu, Zn, Al, C, Li, or N.
- 10 4. A method according to claim 3 in which the invention is introduced in a nominal concentration of between 1 and 5 at .% during a solid state reaction between Mg, B and the additive.
5. A method according to claim 1 in which the structural defects are formed by including an additive chosen on the basis of its inert nature or ability to react with B to 15 form a nano-boride phase of nano particle starting size .
6. A method according to claim 5 in which the additive is introduced in a concentration of 5-15 wt.% during a solid state reaction between Mg, B and the additive.
7. A method according to claim 5 or claim 6 in which the additive comprises Y₂O₃.
8. A method according to claim 4 in which the concentration is 3 at.%.
- 20 9. A method according to claim 6 in which the concentration is 10 wt.%.

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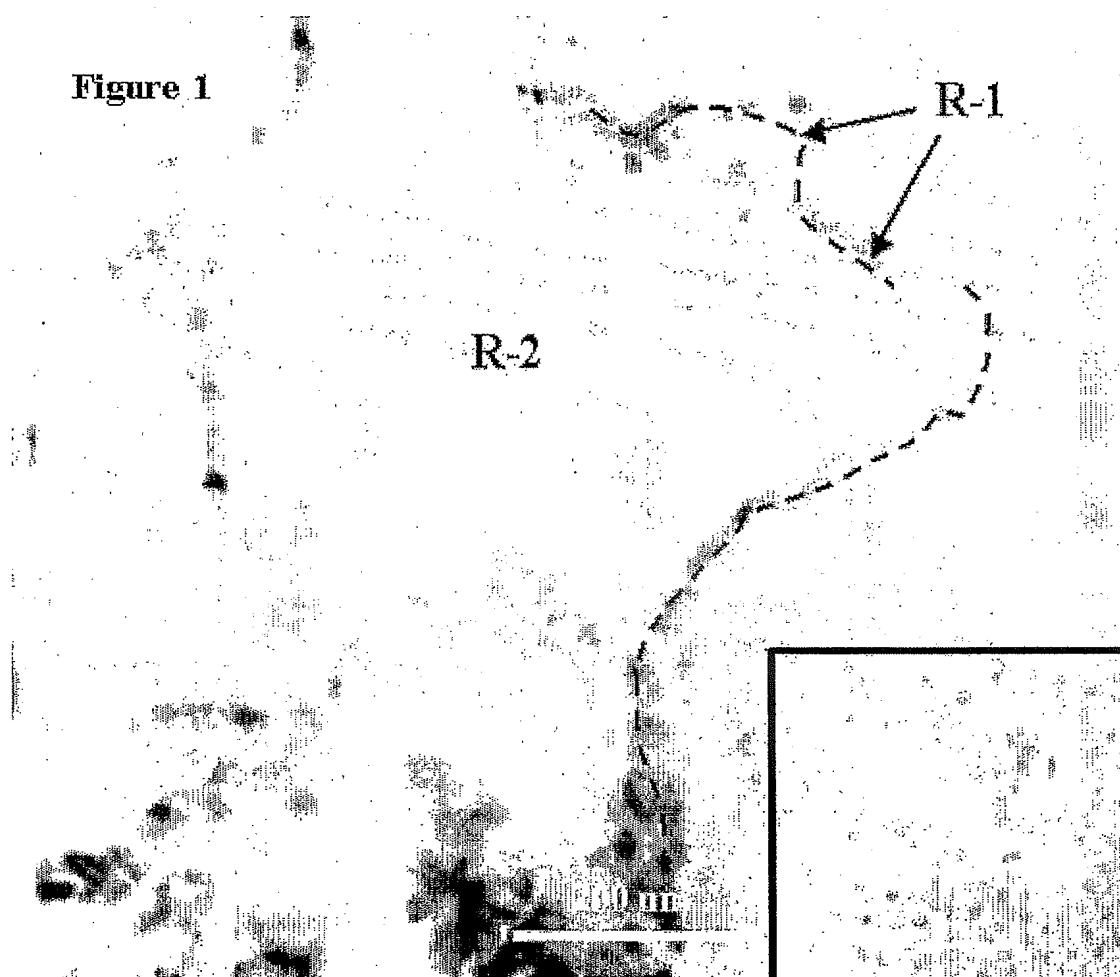
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10. A method according to claim 1 in which structural defects are formed by utilising commercially grade amorphous B powder and annealing for a relatively short time to produce an inherently disordered structure.
11. A method according to any one of the preceding claims in which the materials are mixed, pressed into pellets and then sintered in an inert atmosphere in a reaction which includes annealing in an Mg -rich environment.
12. A method according to claim 10 or claim 11 in which the annealing is performed for 15 minutes at 900°C.
13. A superconducting material comprising bulk polycrystalline MgB₂ made by the method of any one of the preceding claims.

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Figure 1

J_c Normalised at 2T for various doped and undoped MgB₂ samples.

Figure 2

